Raman and SEM Characterization of Electrospun WO_3 Nanofibers

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Abstract

This article reports how the significant it is to recognize the optimal annealing circumstances when electrospun composite fibers are heated to obtain ceramic nanofibers in proper characteristics. Polyvinylpyrrolidone (PVP) and ammonium metatungstate (AMT) nanoscaled fibers have been synthesized by electrospinning aqueous solutions of PVP and AMT. The as-spun fibers and their annealing were studied by scanning electron microscope (SEM) and Raman measurements. The 500 – 600 nm thick and tens of micrometer long PVP/AMT nanoscaled fibers, and pure monoclinic WO_3 nanoscaled fibers formed between 500 and 600 °C. When a high heating temperature (more than 700 °C) was used, the tungsten oxide nanofibers totally disintegrated. When heated at 600 °C, the fibers broke into rods. However, when the annealing temperature was low (500 °C), the nanoscaled fibers morphology was excellent with more crystalline. When the optimal temperature was used, WO_3 nanoscaled fibers with unique morphology and crystallinity were captured. The Raman measurements proved that which this heating parameter the organic matter was completely extracted from the nanoscaled fibers and WO_3 was existing in highly crystalline and ordered form. By Raman scattering investigates we discovered that the films contain hydrates.

Keywords

Nanomaterials; Nanofiber;Tungsten Oxide; Raman Scattering

Introduction

Electrospinning has been recognized as a novel technology that could be applied in the production of functional polymers nano-sized fibers. The method of electrospinning has famous for over 100 years [Zeleny et. al. 1907]. In 1934, the first US patent was discovered [Subbiah, T. et. al., 2005; Chun. I., et. al., 1995; Formhals A., et. al. 1934]. As is well known, the method of electrospinning applies external electrical forces to outcome unique polymeric fibers of diameters in the range from 3 nm to several micrometers [MacDiarmid, A, G. et. al., 2001; Kim. J.S. , 1999, Reneker, D. H. et. al., 1996]. Polymer solution is bringing into nano-sized fibers utilization electrical fields. In addition to orderly polymers, aqueous solution including additives and fillers could be applied to functionalize fibers for apply in distinct utilizations.

Here we show an example investigate on the heat treatment of electrospun polyvinylpyrrolidone [PVP] and ammonium metatungstate [AMT] nanoscaled fibers. It noticeably expresses the vital of discovery the suitable annealing conditions for polymer nanoscaled fibers prepared by electrospinning. We utilize the PVP/AMT nanoscaled fibers as a model system, as we have freshly developed a new electrospinning technique for preparing WO_3 nanoscaled fibers [Szilagyi, I. M. et. al., 2011]. This technology is novel as it is fully water-based, hence eco-friendly and simple to manage, in opposition to the several former studied WO_3 electrospinning methods, which utilized organic solvents to dissolve the polymer and the inorganic precursors [Maensiri, S., et. al. 2006; Lu, X., et. al., 2006]. As reviewed earlier, it was essential to optimize the annealing process of the as-spun PVP/AMT nanoscaled fibers.

Despite the novel properties of WO_3, research on the influence of the oxidation states of WO_3 dependent on the calcined temperature is still lacking. In this study, the PVP/AMT nanoscaled fibers are synthesized by electrospinning aqueous solutions of PVP and AMT. The annealing process of the PVP/AMT fibers and the product WO_3 nanoscaled fibers are characterized by scanning electron microscopy (SEM), and Raman measurements.

Experimental section

The AMT (99% purity) and high molecular weight PVP (M_w : 1,300,000) were used as received. The AMT/PVP nanoscaled fibers were produced by

electrospinning a mixture of aqueous solutions of PVP and AMT. The electrospinning apparatus consisted of a metal needle, a grounded collector, and a high voltage supply [Zhou X. et. al., 2012]. A high voltage of 24 kV was applied to the metal needle tip. The polymer fibers were collected 15 cm from the needle tip during the electrospinning process. An electrically grounded collector was covered with carbon paper.

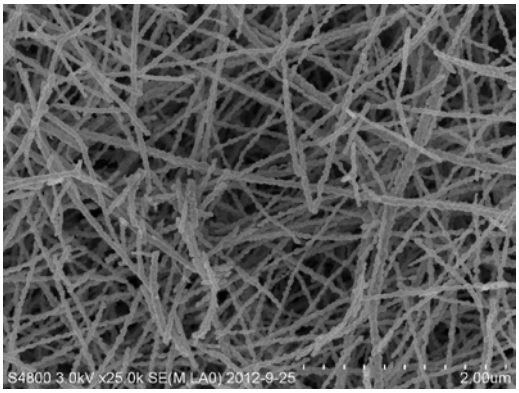
The as-spun nanoscaled fibers were dried in oxygen for 1 hour with a heating rate of 1 °C/min was performed to remove the PVP achieve the crystallization of tungsten oxide. The fibers were heated to 500, 550 and 600 °C. We investigated completely the thermal behavior of the as-spun PVP/AMT nanoscaled fibers in oxygen condition in tube furnace, so that we could ascertain the annealing temperature, where the organic part of the fibers decomposes and burns out totally.

The morphology of the nanoscaled fibers was investigated by a scanning electron microscope (SEM). A Raman measurement was performed at room temperature using Jobin Yvon system. Argon ion (514.5 nm) laser was used as excitation sources for Raman measurement. To focus the laser on the sample surface, microscope objective lenses 100× were employed for Raman measurements [Chuah, L.S. et. al., 2009. Before the Raman measurement, high quality single crystal silicon sample was used to calibrate the system. The full width at half-maximum (FWHM) of the Si Lorentzian peak width was ~ 3 cm^{-1}.

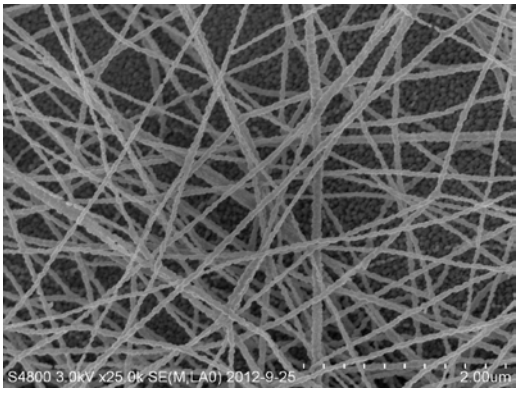
Results and Discussion

Electrospinning of the PVP/AMT polymer solution was satisfied, and having similarity in nanoscaled fibers structure was produced. The PVP could serve as the matrix to host inorganic precursors for preparing ceramic nanoscaled fiber. It is reported that PVP has excellent solubility in alcohols and water. The diameter of the PVP/AMT nanoscaled fibers in the range of 400–600 nm, and the fibers were some tens of micrometers long (FIG. 1*a*). In an oxidizing atmosphere yellow WO_3 is formed. Clearly, the nanofibers WO_3 (500 °C) sample shows fibrous morphology; however, the fibers break seriously (FIG. 1*a*).

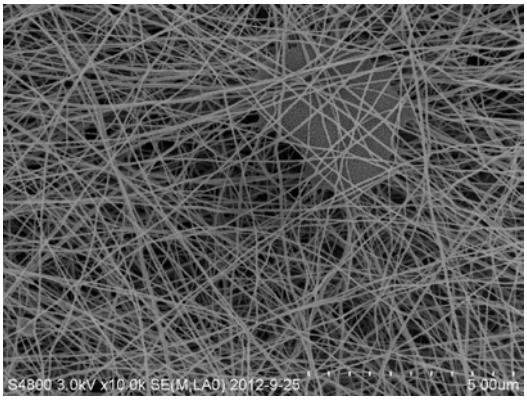
FIG. 2 showed Raman profiles for these three samples. In the present studied, the 514.5 nm wavelength Ar laser was used. Thus Raman peaks of PVA and the precursor could not be found, although the analysis was done over the 100 cm^{-1} to 800 cm^{-1} wavelength range. To detect their peaks, higher wavelength laser should be used, for example 532 nm, 633 nm, and 785 nm.



(a)



(b)



(c)

FIG. 1 SEM IMAGES OF WO_3 NANOFIBERS OBTAINED BY ANNEALING PVP/AMT NANOFIBERS IN OXYGEN AT (A) 600 °C, (B) AT 550 °C AND, (C) AT 500 °C

Seeing that the inorganic compounds have vibrational bands essentially beneath 1200 cm cm^{-1}, a study of Raman spectroscopy of WO_3 nanoscaled fibers was performed in the range the 100 cm^{-1} to 800 cm^{-1}. The first band seat between 200-500 cm^{-1} is linked with *O-W-O* bending vibration modes. According to Bange et. al. [Bange., K. et. al. 1999], they have been studied vacuum deposited tungsten oxide films by mass

spectroscopy. It was revealed that the mass spectrum of the films consists of WO_2, WO_3, W_2O_6, W_3O_8 and W_3O_9 [Nagai, J., 2001]. The bands in the range 750 cm^{-1} is attributed to either the antisymmetric stretch of transition metal (*M*) oxide bonds. The peaks at 316 cm^{-1} are assigned to the bending vibration δ(*O-W-O*) [Cantalini, C., et. al. 1996]. The Raman peak at 280 cm^{-1} was associated to *W-O* bending modes of monoclinic WO_3. Miyakawa has revealed that the Raman bands at 809 and 718 cm-1 were for monoclinic tungsten oxide and did not change as a function of temperature (< 500 deg), indicating the formation of a highly stable monoclinic crystalline WO_3 [Nonaka, K., et. al. 1993].

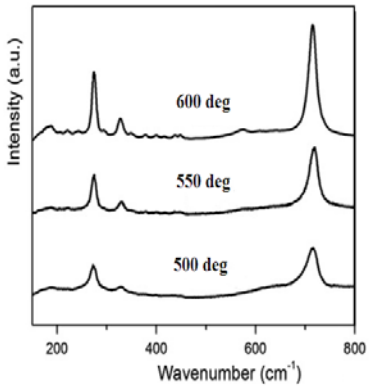


FIG. 2 RAMAN PROFILES FOR SAMPLES AT DIFFERENT DEPOSITION TEMPERATURES

Conclusions

The PVP and AMT composite nanoscaled fibers were synthesized by a lately developed electrospinning method from aqueous solutions of PVP and AMT. Our objective was to perceive the best optimum annealing situations of the PVP/AMT fibers to obtain high quality WO_3 nanofibers. The sample prepared under high substrate temperature was also investigated. The diameter and length of the nanostructure samples growth up by increasing the substrate temperature. The progression of surface morphology was notable, when in fact the structure was quite stable.

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